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Fabrication of specimens of metamorphic magnetite crystals for field ion microscopy and atom probe microanalysis

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Abstract

Field ion specimens have been successfully fabricated from samples of metamorphic magnetite crystals (Fe_3O_4) extracted from a polymetamorphosed, granulite-facies marble with the use of a focused ion beam. These magnetite crystals contain nanometer-scale, disk-shaped inclusions making this magnetite particularly attractive for investigating the capabilities of atom probe field ion microscopy (APFIM) for geological materials. Field ion microscope images of these magnetite crystals were obtained in which the observed size and morphology of the precipitates agree with previous results. Samples were analyzed in the energy compensated optical position-sensitive atom probe. Mass spectra were obtained in which peaks for singly ionized ^{16}O, ^{56}Fe and ^{56}FeO and doubly ionized ^{54}Fe, ^{56}Fe and ^{57}Fe peaks were fully resolved. Manganese and aluminum were observed in a limited analysis of a precipitate in an energy compensated position sensitive atom probe.

Keywords: Oxide; Magnetite; Field ion microscopy; Atom probe microanalysis; Focused ion beam; Sample preparation

1. Introduction

The frontiers of geology and astrobiology are constantly pushing the limits of detection of elemental distributions to ever finer scales. Atom probe field ion microscopy (APFIM) is a highly attractive technique in these fields despite the inherent difficulties in analyzing semiconducting and insulating materials. The local electrode atom probe (LEAP) shows potential for overcoming some of the difficulties in analyzing low conductivity samples as well as a reduction in the steps required for sample preparation [1]. The National Aeronautics and Space Administration (NASA) is developing a prototype miniature local electrode atom probe (Mini-LEAP) at the Jet Propulsion Laboratory (JPL) for in-situ implementation in remote and extraterrestrial environments.

In conjunction with the development of the Mini-LEAP, a conventional APFIM study of several minerals has been initiated. A previous attempt to study rutile (TiO_2) has shown how

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difficult mineral samples are to prepare for the APFIM analysis [2]. In the current work, field ion tips were fabricated from samples of metamorphic magnetite (Fe_3O_4) crystals extracted from a poly-metamorphosed, granulite-facies marble with the use of a focused ion beam (FIB) milling system [3–5]. This particular magnetite was chosen for several reasons. First, magnetite is a common mineral on Earth and Mars. Second, magnetite is one of the more conductive minerals, having a resistivity of $52 \times 10^{-4}\,\Omega\,\mathrm{cm}$ [6]. Finally, this particular magnetite contains disk-shaped precipitates approximately 40 nm in diameter, 1–3 nm thick and about 10^4 platelets/μm^3 [7,8]. Qualitative energy-dispersive X-ray spectroscopy (EDXS) has shown that manganese is concentrated in these precipitates and aluminum may also be present. However, quantitative analysis has been limited by the thickness of this second phase. The precipitates may also assist in maintaining the mechanical integrity of the samples, mitigating the fracture mechanisms that have made parallel analyses of single-crystal rutile unsuccessful. These considerations make this magnetite particularly attractive for investigating and demonstrating the capabilities of the APFIM for geological materials.

2. Sample preparation

Camus, Melmed and Banfield introduced the method of sharp shards (MSS) in 1991 for preparing non-conductive samples that are not amenable to chemical etching [2]. The current work takes advantage of recent advances in the FIB technology to more precisely shape and sharpen relatively non-conductive samples [4] than is possible with the MSS alone. Note that all images in this paper have been taken on one particular sample of magnetite, 031300E, unless otherwise stated, to illustrate the process of reducing a macroscopic rock to a field ion specimen suitable for the APFIM analysis.

2.1. Method of sharp shards

The extracted metamorphic magnetite crystals averaged approximately 1–2 mm in diameter and were randomly crushed to make shards less than 200 μm in length. These shards were placed on a glass microscope slide and selected based on length and shape with a stereoscopic microscope. The tip of a stainless steel insect pin mounted in copper tube was carefully loaded with a small amount of two-part, conductive silver epoxy. Micromanipulators were used to mount a suitably shaped fragment to the pin. The fragment was then carefully straightened with an electropolished wire probe on a micromanipulator (Fig. 1). Colinearity of the shard axis and the pin axis were found to be critical for successful analysis in the atom probe due in part to the limited range of motions of the specimen stage in an energy compensated position sensitive atom probe (ECOPoSAP). This colinearity also provides for the fabrication of a longer sample, facilitating resharpening of the tip.

2.2. Coatings

Coatings have previously been deposited on non-conductive samples for the APFIM analysis

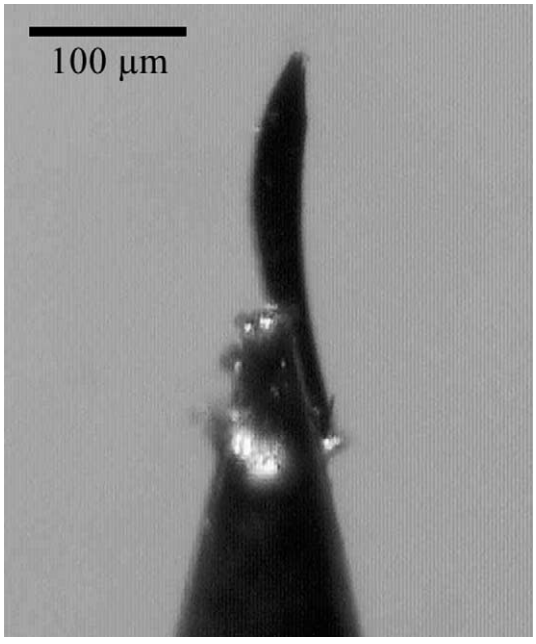

Fig. 1. The optical micrograph of magnetite sample 031300E mounted using the MSS. The magnetite fragment is attached to a stainless steel insect pin using two-part, conductive silver epoxy.

to improve the electrical properties of the samples [9]. Early samples in the current study were sputter-coated with ~50 nm of Cr after tip fabrication. Analysis of the sample tips after Cr deposition demonstrated a lack of control in achieving a uniform thin coating on a feature with a high aspect ratio. Although Pt is not generally the first choice of coating materials due to its low vapor pressure and high evaporation field, the ion-assisted deposition of Pt traces is easily accomplished in the FIB. Platinum traces were deposited on later samples along the sides of the sample and between the sample and the stainless steel pin in an attempt to improve the conductivity of the sample (Fig. 2a). The Pt traces were generally several micrometers in width, up to 100 μm in length and ~200 nm thick. Platinum was also deposited to fill in holes and craters created during the fabrication process. It is not clear if the Pt deposition improved the quality of the specimen because of the number of other variables involved in sample failure during atom probe analysis. However, it is thought that non-conductive samples require coating to maintain conduction to the tip. These Pt traces might also improve the mechanical integrity of the samples during analysis, but this has not yet been verified.

2.3. Focused ion beam milling

Shaping of the sample is a time-intensive effort. Once the epoxy had cured overnight, the samples were loaded into an FEI 600 FIB capable of 25 keV Ga beam currents up to 4000 pA and equipped with an ion-assisted platinum deposition system. Sample 031300E prior to milling with the FIB is shown in Figs. 1 and 2a. The sample after the removal of a considerable amount of material is shown in Fig. 2b. The shaping was accomplished by gross milling with high beam currents, followed by progressively finer milling with decreasing beam currents near the tip. Some samples have shown evidence of melting due to high beam currents. This observation led to the adoption of smaller beam currents near the tip, increasing the sample preparation time. Once the basic shape of the tip

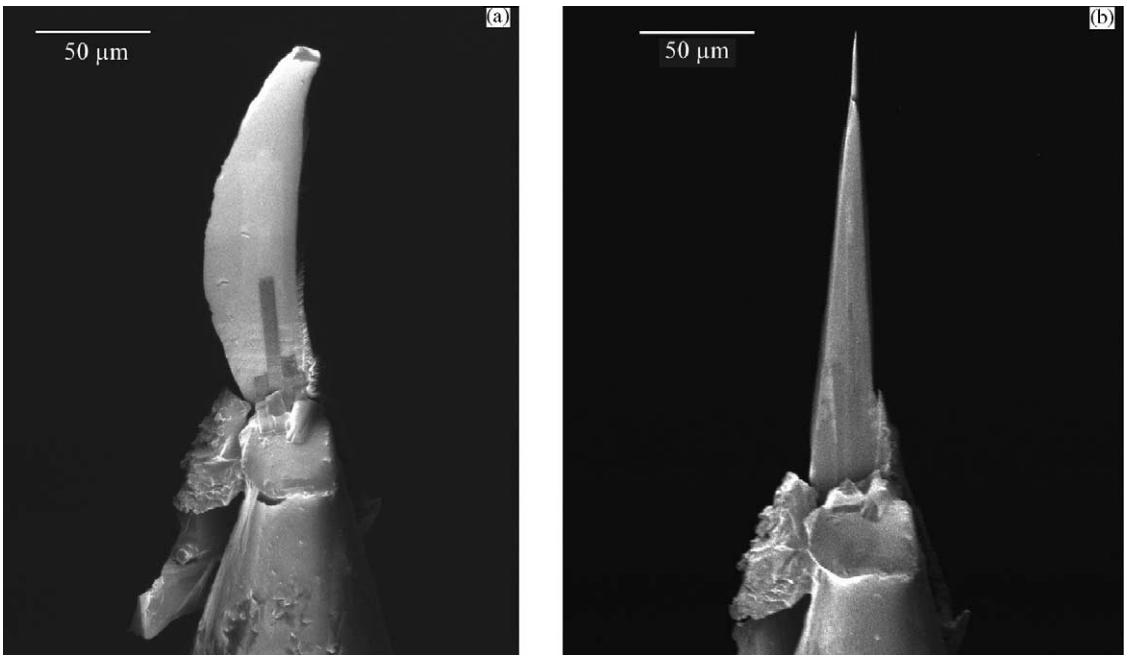

Fig. 2. The FIB induced secondary electron images of magnetite sample 031300E. (a) Sample as mounted with Pt deposition at the base to improve electrical connection. (b) Sample after extensive ion milling using various beam currents.

had been achieved by a series of cuts, the sample was tilted so that its major axis was parallel to the beam direction. An annular milling pattern was generated based on the diameter of the base of the sample to reduce the amount of cratering around the circumference of the shank of the sample. Such cratering introduces potential points for mechanical failure. The initial annular milling was done with a relatively high beam current ($\sim$1000 pA). The interior hole of the pattern, where no milling occurs, was made progressively smaller to carve out a round tip. The beam current was reduced to 16 pA for the final shaping cut. Some circumferential cratering was unavoidable and was minimized by tilting the sample and removing extraneous protrusions while the sample was in profile. Fig. 2b shows the sample after final annular milling. Note that some of the Pt traces remain at the base of the magnetite after milling because the FIB allows for fine control of the beam size and location

The prepared samples were examined in the Phillips CM30 transmission electron microscope (TEM) at ORNL operated at 300 keV. Fig. 3 shows sample 031300E after preparation with the FIB was completed. The radius of curvature of the tip is approximately 25 nm. As the tip was fabricated by sputtering the sample with 25 keV-Ga^+ ions, implantation of Ga is of great concern. The extent of damage caused by this implantation is illustrated in Fig. 3b. An amorphous layer $\sim$10 nm thick at the tip and decreasing in thickness along the shank was created during the FIB milling. However, the sample was sufficiently sharp that this damaged layer was field evaporated prior to the APFIM analysis.

2.4. Sample recovery

After ion milling in the FIB, a sample with suitable geometry (such as shown in Figs. 2b and 3a) could be milled in a dual beam ion mill to

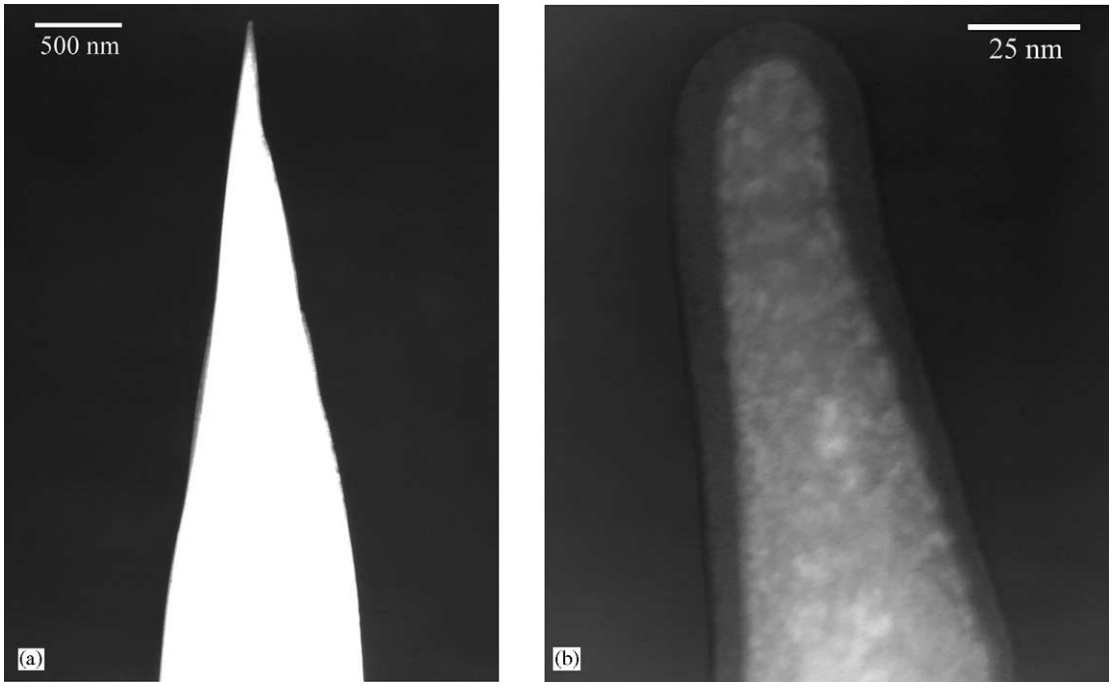

Fig. 3. The transmission electron micrographs of sample 031300E after preparation with the FIB. (a) Profile of tip illustrating the smooth shank obtained. (b) Sample tip showing probable radiation damage due to the 25 keV Ga beam. Note that the damage decreases in thickness further down the shank of the sample.

Fig. 4. The transmission electron micrograph of sample 031300E after analysis in the ECOPoSAP. Note the slight roughness at the tip.

resharpen the tip if desired. The tip shown in Fig. 4 was milled in a Gatan ion mill with a 5 keV Ar beam at an angle of 50° from the sample axis (gun tilt = 40°) for 30 min to produce the tip shown in Fig. 5. The particles on the side of the sample appear to be electrostatically held and did not interfere with the APFIM analysis. This particular sample was resharpened twice and analyzed in the APFIM, demonstrating the ability to perform multiple analyses on a single sample with minimal additional sample preparation.

3. Experimental analysis

Finished samples were introduced into the ECOPoSAP and cooled to 60 K. The base pressure for the APFIM analyses was $<1.0\times10^{-10}$ mbar. The samples were initially imaged with Ne as the imaging gas at a pressure of $\sim1.3\times10^{-5}$ mbar. The specimens were field evaporated until a full FIM image was achieved. A pulse fraction of 20% and a pulse repetition rate of 1500 Hz were used for the atom probe analyses.

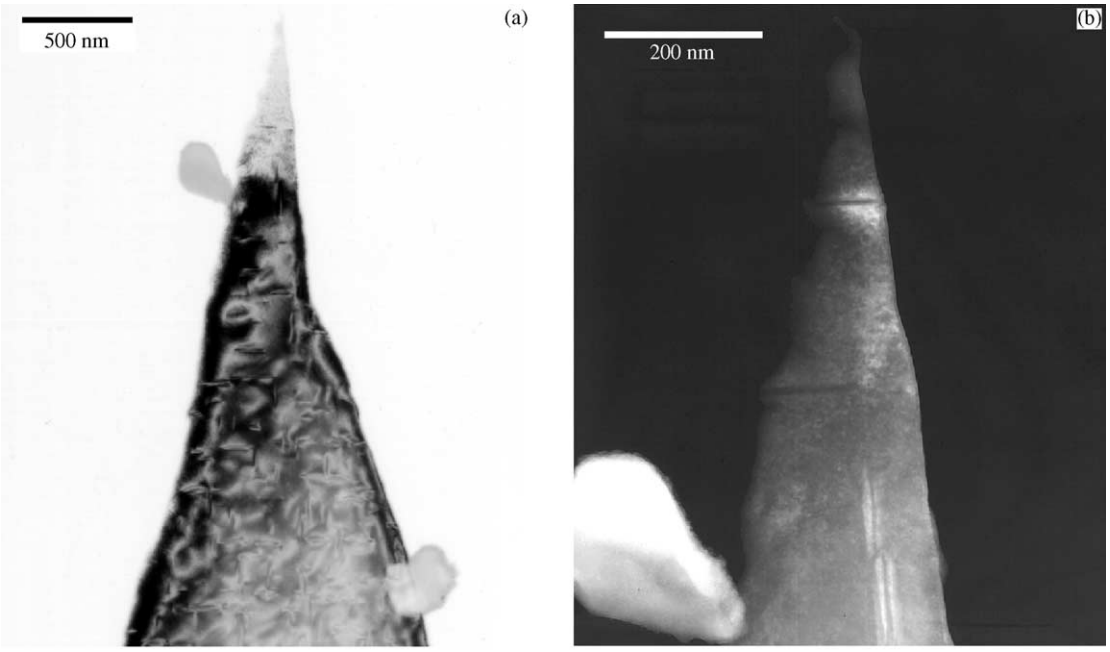

Fig. 5. The transmission electron micrograph of sample 031300E after resharpening with a Gatan ion mill with 5 keV Ar and gun tilt = 40°. (a) Bright field image showing precipitates and bend contour. (b) High magnification image of the tip.

4. Results

Good quality field ion images of this specimen were obtained as shown in Fig. 6. These field ion micrographs of sample 031300E reveal precipitates as thin dark bands and two distinct crystallographic poles. Two of the precipitates seen in the FIM images, Fig. 6, were also visible in the TEM dark field images, Figs. 5 and 7, acquired prior to and after field evaporation, respectively. Several samples of magnetite field evaporated uniformly until the voltage limit of the atom probe was reached. This result indicates that Pt-coated magnetite has sufficient electrical conduction and mechanical strength for field ion microscopy (FIM) characterization of this material.

Occasionally, a specimen would continue to field evaporate when the applied voltage was reduced below the best image voltage, indicating a charging phenomena. In addition, many specimens failed during atom probe analysis. Examination of sample 031300E after the initial atom probe analysis revealed it did not have a smooth, rounded surface typical of field evaporated tips indicating a slight fracture, as shown in Fig. 4.

The maximum number of positioned atoms collected to date from magnetite in this study is $\sim$2500 ions. A mass spectrum representative of the matrix magnetite is shown in Fig. 8 and is made up of 2267 positioned ions. Both singly and doubly charged single ions of all the isotopes of Fe and O were collected as well as singly and doubly ionized clusters of FeO complex ions. The mass resolution obtained was comparable with metallic specimens. As with metallic specimens, hydrogen appears in the mass spectra as H^+, H_2^+ and H_3^+. An increase of two orders of magnitude in the number of atoms collected is essential for quantification of the composition of the magnetite and precipitates. The use of a pulsed laser to field evaporate the specimen may enable more data to be collected. However, this option is currently not available.

Sample 031300E was sharpened a third time with 5 keV Ar^+ and analyzed in the ECOPoSAP. A mass spectrum was obtained from an area of the FIM image that contained a precipitate. This spectrum shows the presence of both Mn and Al, as expected [7]. However, the limited number of ions did not allow a quantitative analysis of the composition of these precipitates.

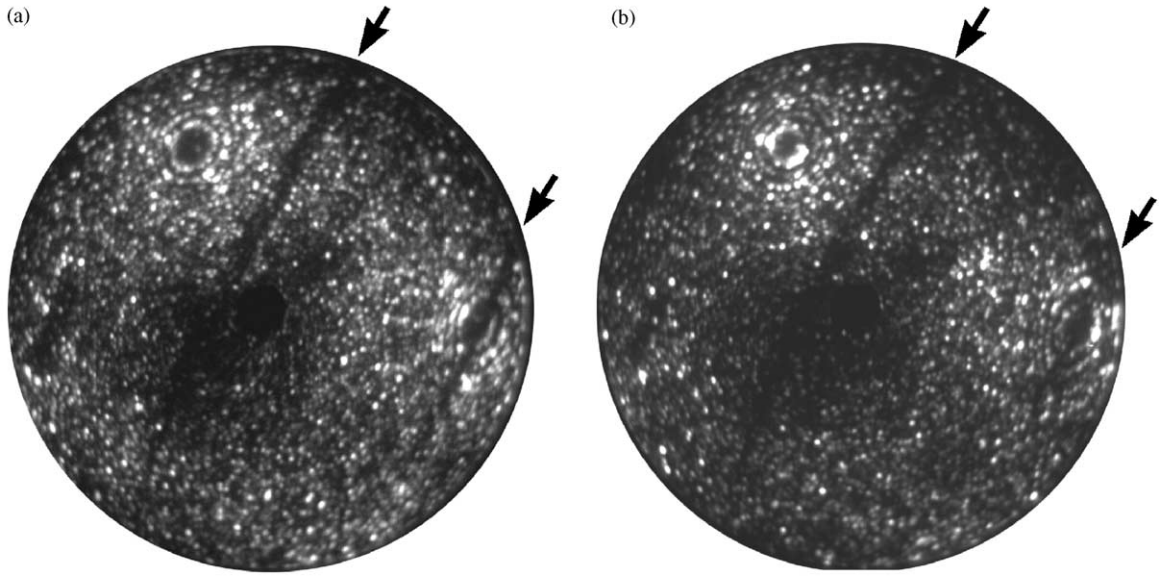

Fig. 6. The field ion micrographs of magnetite LP204-1 and oriented precipitates (indicated by arrows) at (a) approximately 16 kV and (b) 16.5 kV. Note the clarity of the {1 1 1} poles and the precipitate running directly through the pole at the right of the images.

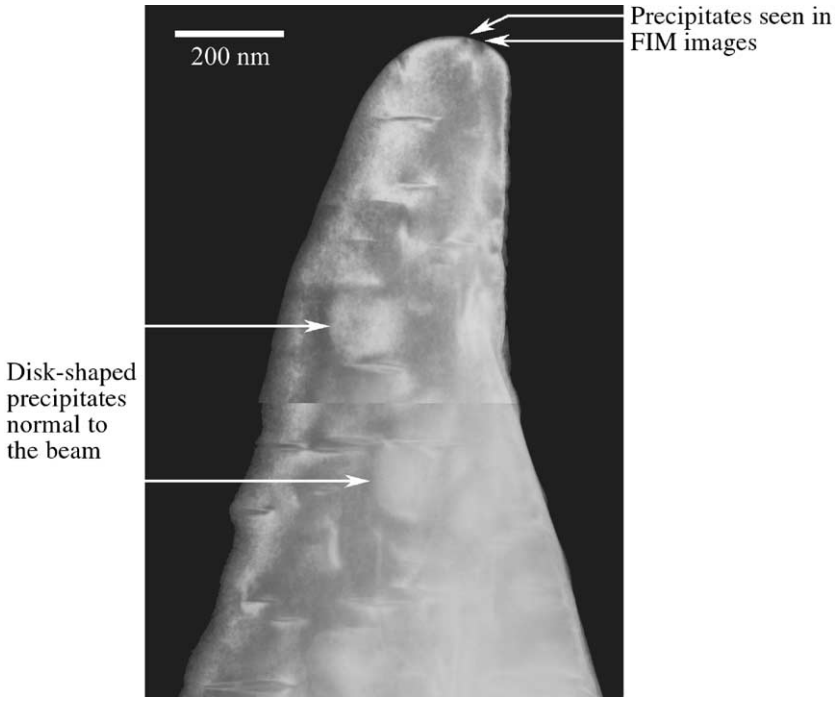

Fig. 7. The transmission electron micrograph montage of sample 031300E after the FIM analysis in the VG APFIM at ORNL. Note the correlation between the "knee" in the right side of this image and Fig. 5a. Also, note the light disks of precipitates approximately 180 nm in diameter near the center of the image.

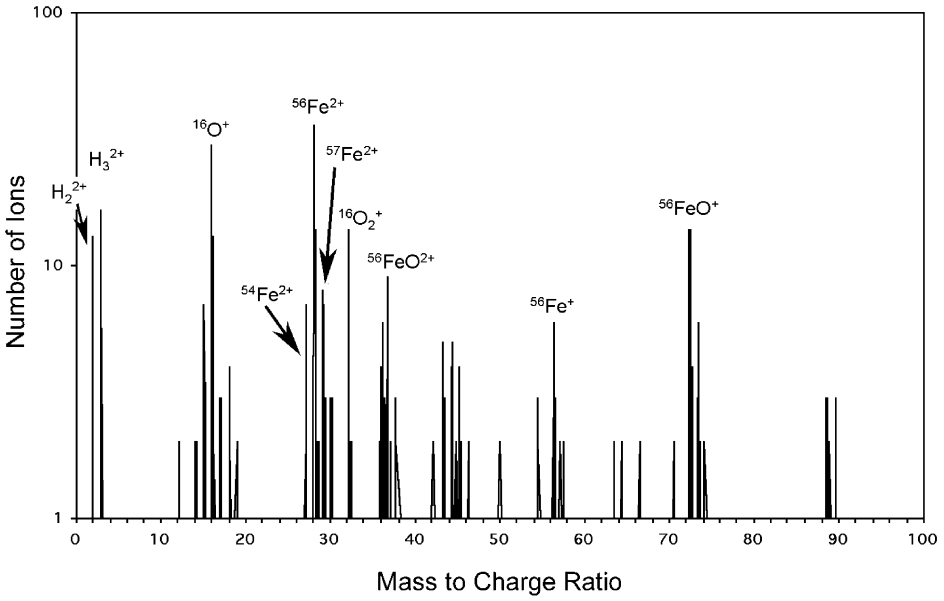

Fig. 8. The preliminary mass spectrum of the matrix in magnetite, LP204-1. This spectrum contains 2267 atoms.

5. Conclusions

The first high quality FIM images and preliminary APFIM analysis of magnetite are reported. This study demonstrates that with careful sample preparation, magnetite can be imaged by conventional FIM and shows potential for the analysis of mineral specimens in the atom probe. Mass spectra have been obtained showing isotopes of Fe and O as well as FeO. Both singly and doubly charged ions are observed. A preliminary mass spectrum taken from a precipitate in the third analysis of 031300E contains both Mn and Al, as expected from previous analysis of magnetite LP204-1. Three-dimensional analysis of magnetite containing precipitates has been limited due to data sets of less than 2500 positioned atoms.

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